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Reaction of metallic iron and copper sulphate in the flotation of sphalerite

Charles Wilson Ambler

Department:

REACTION OF METALLIC IRON AND COPPER SULPHATE IN THE FLOTATION OF SPHALERITE.

- By -

C. W. Ambler, Jr.

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THESIS

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Supervising Engineer,
Mississippi Valley Experiment Station,
United States Bureau of Mines.

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P R E F A C E.

This thesis is presented to the Faculty of the Missouri School of Mines and Metallurgy of the University of Missouri in partial fulfillment of the work required for the degree of Master of Science.

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REACTION OF METALLIC IRON AND COPPER SULPHATE IN THE FLOTATION OF SPHALERITE.

- By -

C. W. Ambler, Jr.

INTRODUCTION.

Copper sulphate is a common flotation reagent for blende ores. Metallic iron is also present in the mill circuit and a reaction between the iron and the salt would be in accord with well known chemistry. The abundance of metallic iron in a flotation feed may be noted by the examination of any feed. It originates, first of all, in the mine, then the coarse crushing machines contribute their share, and finally the fine grinding medium is a large contributor. If the grinding is with cast iron balls the amount of metallics is greater than when steel is used. In the end much more metallic iron is present than would be indicated by noting the ball consumption. An estimate that the total amount of metallics is twice that supplied by the balls and liners might not be far amiss.

It is well known that copper sulphate plates out on iron in an acid solution, but since flotation is common in solutions where acid has not been added this reaction has not been given due thought.

Its importance may be better understood when it is realized how great is the tonnage of zinc ores now being treated by flotation in this country. According to Gaudin[1] 5,536,244 tons of zinc

[1] Gaudin, A. M., Consumption of reagents used in flotation, 1927. U. S. Bureau of Mines Report of Investigation No. 2931.

ore were treated by flotation during 1927. In all of these operations copper sulphate was employed as an activating agent, the amount per ton averaging 0.81 pound for straight sulphide zinc ores and 1.16 pounds for complex ores. Since such large quantities of zinc ore are treated by flotation, and since metallic iron is always present, it is of importance to study their reactions upon each other, and the effect of their reaction products upon flotation.

METHOD OF CONDUCTING FLOTATION EXPERIMENTS.

The sample used was a clean sphalerite ore from the Tri-State District of Missouri, Kansas, and Oklahoma. All the iron metallics resulting from crushing at the mine and in the laboratories were removed and natural slimes were absent.

A suitable ore having been closen, a procedure was worked out which gave excellent flotation results when metallic iron was absent. This procedure consisted of grinding 525 grams of the ore in an Abbé pebble mill with chert pebbles so that contamination with metallic iron was avoided. The Abbé pebble mill is shown in Figure 1. The reduction was 80 per cent through 200 mesh. The

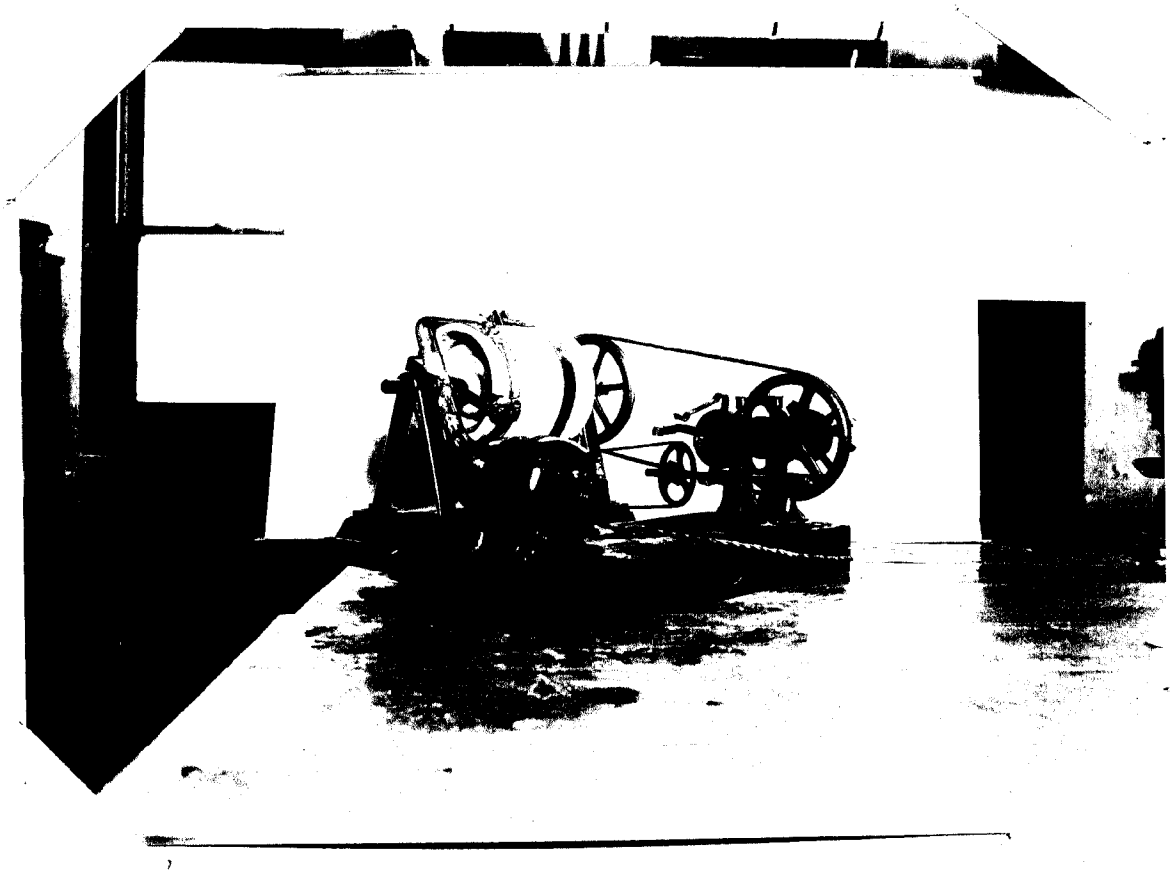

Figure 1.

Abbé Laboratory Pebble Mill.

pulp was treated in a cell of the minerals separation type, shown in Figure 2. Ordinary tap water was used to give a pulp density of approximately 20 per cent.

One of the analyses of the tap water is given on Page 10. It was the kind likely to be met in any flotation practice.

Flotation Tests After 5-Minute Conditioning Period in the Presence of Varying Amounts of Iron.

The ore pulp was conditioned for five minutes with the equivalent of 1.2 pounds of anhydrous copper sulphate. For flotation the following reagents were added:

	Pounds Per Ton
Sodium ethyl xanthate	0.28
Steam distilled pine oil	.24
Copper sulphate (anhydrous)	.80

(Copper sulphate – 2.00 pounds per ton).

When metallics were absent the ore was remarkably amenable to concentration; the recovery was 98.0 per cent and the concentrate assayed 60.0 per cent zinc.

The iron used had been prepared by precipitating with hydrogen and pulverizing. It was added to the ore in the pebble mill and ground with it. The amount varied from 0 to 14 pounds per ton of ore.

Figure 2.

Laboratory Flotation Machine (Minerals Separation Type).

The results of this series of tests are given in Table I. The grade of concentrate remained practically the same in all cases, averaging 60.0 per cent zinc, but the percentage of zinc remaining in the tailings increased progressively from approximately 2 per cent, where no metallic iron was added, to a maximum of 7.5 per cent for the greatest amount of metallic iron (14 pounds per ton of ore). When the amount of iron was normal, say 3 pounds, the ill effect was not notable with 2 pounds of copper sulphate per ton of ore.

The conditioning period was then extended to 10 minutes.

Flotation Tests After 10-Minute Conditioning Period in the Presence of Varying Amounts of Iron.

In this series of experiments the procedure was the same as that in the first series, except that the conditioning period was increased from 5 to 10 minutes. The data obtained are given in Table II. The results are not materially different from those of the preceding series when the conditioning period was only 5 minutes.

Table I. Flotation Tests After 5-Minute Conditioning Period With Copper Sulphate in the Presence of Varying Amounts of Iron.

Pounds of Iron Per Ton of Ore	Assay Per cent Zinc		Per cent Total Zinc in Tailings
	Concentrate	Tailings	
0.0	60.2	0.13	1.89
0.0	59.9	.15	2.06
2.0	61.6	.15	2.33
2.0	61.6	.12	1.63
4.0	60.9	.14	2.12
4.0	60.6	.15	2.29
6.0	59.2	.12	2.13
6.0	59.6	.20	3.60
6.0	60.8	.27	4.00
6.0	61.9	.19	3.47
6.0	58.2	.17	3.22
6.0	59.4	.13	2.69
6.0	58.9	.18	3.54
6.0	61.9	.20	2.87
8.0	60.8	.34	4.53
10.0	59.8	.29	4.80
10.0	60.4	.25	4.80
14.0	61.6	.44	7.50

Table II. Flotation Tests After 10-Minute Conditioning Period With Copper Sulphate in the Presence of Varying Amounts of Iron.

Pounds of Iron Per Ton of Ore	Assay Per cent Zinc		Per cent Total Zinc in Tailings
	Concentrate	Tailings	
0.0	60.5	0.08	1.1
0.0	60.0	.06	.9
2.0	62.0	.18	2.7
2.0	60.6	.10	1.5
2.0	62.1	.14	1.9
4.0	61.6	.11	1.5
4.0	61.9	.14	1.9
6.0	61.3	.20	3.7
6.0	62.5	.24	3.6
6.0	60.7	.18	2.6
6.0	61.3	.15	2.2
8.0	61.0	.18	3.0
8.0	60.6	.20	3.1
8.0	61.4	.24	3.6
10.0	63.6	.27	5.0
10.0	61.4	.21	3.7
10.0	61.4	.20	4.1
12.0	61.7	.36	6.4
14.0	61.9	.71	14.2

A third series of tests with the amount of copper sulphate increased from 2 to 4 pounds was then made.

Flotation Tests Employing 4 Pounds of Copper Sulphate Per Ton of Ore in the Presence of Varying Amounts of Iron.

The procedure was the same as that employed in the first two series except that the amount of copper sulphate was doubled. The total amount of the salt used in each test was the equivalent of four pounds of the anhydrous salt per ton of ore. The results of these tests are shown in Table III, where it may be seen that the effect of the iron is more pronounced.

In all of the experiments in which metallic iron was added to the flotation pulp, the losses of sphalerite are markedly higher than in the preceding series of tests where a smaller amount of copper sulphate was used. That this decrease in the recovery of sphalerite is not due to any deleterious effect of the copper sulphate itself is evident by noting the results of the test in which the increased amount of copper sulphate was used, but in which no metallic iron was added. In this test the recovery of the zinc was high and compared closely to those obtained in like tests of the preceding series. However, in the tests with 4 pounds of copper sulphate, where metallic iron was added to the flotation pulp, the amount of sphalerite remaining in the tailing increased rapidly and progressively, reaching a maximum for the greatest quantity of iron, 12 pounds per ton. When the

Table III. Flotation Tests Using 4 Pounds of Copper Sulphate Per Ton of Ore in the Presence of Varying Amounts of Iron.

Pounds of Iron Per Ton of Ore	Assay Per cent Zinc		Per cent Total Zinc in Tailings
	Concentrate	Tailings	
0.0	58.2	0.09	1.5
2.0	61.4	.30	4.4
4.0	59.6	.15	2.7
4.0	61.2	.44	6.5
4.0	60.6	.19	2.8
4.0	61.1	.19	2.4
6.0	60.3	.20	8.0
6.0	61.4	.76	11.0
6.0	60.9	.55	8.0
6.0	60.4	.67	9.4
8.0	61.6	.92	14.2
8.0	61.6	.95	14.3
12.0	62.0	1.15	23.0
12.0	61.4	.95	17.2

maximum was used the percentage of zinc remaining in the tailing amounted to approximately 20 per cent, whereas less than 2 per cent remained where no iron was used.

It therefore seemed evident that the only explanation for the losses of the sphalerite in the flotation circuit containing both metallic iron and copper sulphate was that a reaction occurred between the iron and the copper sulphate with the consequent formation of a deleterious salt. A study was then undertaken to determine the nature of the reactions taking place.

BEAKER TESTS WITH COPPER SULPHATE AND WATER.

When copper sulphate was added to the alkaline water it was completely precipitated until the amount of copper sulphate was sufficient to make the solution acid. Beyond the point of acidity a precipitate continued to form while a part of the copper sulphate remained in solution. Doubtless this reaction is similar to that of ferrous sulphate when it is employed in its popular role as a water purifier.

The salts formed by the addition of small amounts of copper sulphate were a complex basic copper carbonate, having the general formula $CuCO_3 \times Cu(OH)_2$, and $CaSO_4$. The value for x varies with the amount of copper sulphate added and with the temperature, the CO_3 radical breaking down into CO_2 and OH ions progressively as the temperature of the solution is increased. At 90° C. the conversion of carbonate to hydrate was complete.

The water used in all the experiments was Missouri School of Mines tap water from deep wells. This water is slightly alkaline, having an hydrogen ion concentration of 7.5 and contains considerable calcium and magnesium bicarbonate. One of the analyses of it is as follows:

ANALYSIS OF TAP WATER.

Positive Radical		As Hydrogen Equivalents	As Parts Per Million
Na		0.469	10.8
Ca		2.48	49.7
Mg		2.53	30.7
Fe		0.03	.8
	Total	5.509	92.0
Negative			
Cl		0.144	5.1
NO_3		0.218	13.5
SO_4		0.557	26.7
CO_3		0.468	10.3
HCO_3		4.41	269.1
	Total	5.797	324.7

Error in determination $\frac{5.797 - 5.509}{5.797 + 5.509} \times 100 = 2.55$ per cent.

The analysis shows 4.41 hydrogen equivalents of bicarbonate as the chief constituent of the negative radicals, that is equivalent to 269.1 p. p. m. An expression of the probable composition of some of the salts formed in the flotation cell was undertaken.

PROBABLE FORMULA OF SOME OF THE PRECIPITATED SALTS IN FLOTATION.

Copper sulphate was added to tap water in the proportion that would be present in the flotation cell when 4 pounds per ton of ore was used in a 4 to 1 pulp. The resulting solution was slightly acid, having a pH value of 6.3, some of the copper sulphate remaining in solution, the remainder being precipitated as a basic salt having the following analysis:

Cu - 49.8 per cent

CO_2 - 14.0 per cent

SO_4 - 5.5 per cent

CaO - 3.1 per cent

H_2O - 18.0 per cent.

It is believed that the Ca and SO_4 radicals were present as $CaSO_4$, and that the formula for the other salt formed was approximately $CuCO_3$ 3 Cu $(OH)_2$.

FLOTATION TESTS WITH PRECIPITATED COPPER SALTS.

The insoluble salts were effective in the flotation of sphalerite as was proved by using them in the place of copper sulphate in the flotation circuit. When quantities of the precipitated salt were added to the flotation circuit the results obtained were similar to those using copper sulphate, if equivalent quantities of copper are used in each case. The results of the flotation tests in which the precipitated copper salt was used instead of copper sulphate as the activating agent, are given in Table IV.

When no metallic iron was present only 2 per cent of the sphalerite remained in the tailing. The losses of sphalerite increased moderately as the larger amounts of metallic iron were added. When 12 pounds of iron per ton was added the amount of sphalerite left in the tailing was 7 per cent. Of course the pulp remained alkaline because the acid reacting copper sulphate was not used.

Although the salt formed by the reaction of the copper sulphate and tap water has been called insoluble, this is not strictly true. From its behavior in the flotation cell, it is apparent that the salt is slightly soluble, allowing it to react with other substances.

Table IV. Flotation Tests with Precipitated Copper Salt and Varying Amounts of Metallic Iron.

Pounds of Iron Per Ton of Ore	Assay Per cent Zinc		Per cent Total Zinc in Tailings
	Concentrate	Tailings	
0.0	58.2	0.17	3.2
0.0	56.2	.08	1.4
2.0	59.2	.16	2.6
2.0	60.3	.10	1.7
4.0	59.7	.28	4.8
4.0	56.6	.15	2.3
6.0	56.1	.25	5.3
8.0	57.2	.23	4.5
10.0	57.2	.33	7.5
12.0	56.3	.41	7.1

REACTION OF COPPER SALTS AND METALLIC IRON.

Copper salts and metallic iron were believed to react in the flotation circuit. Experiments were accordingly made to examine this theory.

Amounts of copper sulphate, tap water, and metallic iron were taken in a beaker in the same proportion as in the flotation test in which 4 pounds of metallic iron and 4 pounds of copper sulphate were present. The mixture was agitated for 30 minutes. Then the precipitate and metallic iron were removed by filtering. The filtrate was found to have a pH value of 6.8 and to contain iron and copper. The residue contained iron and copper salts, particles of metallic iron covered with a coating of metallic copper, and particles of sponge copper. Upon standing the iron salts hydrolyzed, forming either basic iron sulphate or hydroxide, and carried down with them all the copper that had been in solution. The pH of the solution after standing became 6.4.

Similar tests made in a flotation cell with ore present gave somewhat different results, due to a slight alkalinity of the ore. The pH value of the pulp after grinding was 7.8, whereas the fresh water was 7.5. Metallic iron when ground with the ore did not have any effect in changing the alkalinity. Copper sulphate was added to the pulp and conditioned for 5 minutes, at the end of which time the pulp had a pH value of 6.8. Xanthate and pine oil were added and the sphalerite floated. At the end of the frothing

period the pH value came back to 7.8. No copper or iron salts were present in solution at this time. It seems logical to assume that any of the soluble iron salts formed through the reaction between the copper salts and metallic iron were hydrolyzed almost as soon as formed and took any remaining copper sulphate out of the solution.

A similar test using 2 pounds of copper sulphate instead of 4 pounds showed that this amount of copper sulphate was not sufficient to make the pulp acid. After grinding the ore, adding the copper salt, and conditioning for 5 minutes the pulp had a pH value of 7.4.

The pH value of the pulps after the addition of copper sulphate seems to indicate why the flotation tests in which 4 pounds of the salt were added gave poorer results than when 2 pounds were used. The pulp in the first test was slightly acid and in the other slightly alkaline after the copper sulphate was added. While all facts point to a reaction between metallic iron and copper sulphate in slightly alkaline pulps, there is no doubt but that this reaction takes place much more rapidly and more completely when the solution becomes acid.

From the flotation experiments made with no metallic iron present it was evident that copper sulphate to the extent of 4 pounds per ton could be used without its excess being injurious to the flotation of sphalerite.

The progressive detrimental effect of iron as the amount of iron is increased can only be explained by stating that the reaction between copper salts and metallic iron is progressive and depends upon the surface area of the iron. The detrimental effects on the flotation of sphalerite are believed to be due to the precipitation of copper and to the formation of iron salts. Ferrous sulphate is probably formed first, but due to the aerating action of the flotation cell it is soon hydrolyzed and precipitated as the hydroxide or as a basic iron sulphate.

No claim is made for new truths in this paper. It is only intended to translate some of the most elementary chemistry into flotation nomenclature.

CONCLUSIONS.

1. Copper sulphate is known to plate out on iron in an acid solution, but this reaction has not been given much thought in the flotation of zinc ores because acid is not used. If the metal does plate out a loss of its flotative effect would be expected.

2. A clean Tri-State zinc ore was ground so that iron metallics were avoided. When 2 pounds of copper sulphate per ton of ore was used, 6 to 14 pounds of metallics had to be added before the ill-effect of the iron was noticed. But when 4 pounds of the salt was used the injurious effect of the iron was more pronounced.

3. The tests were made in tap water that had an alkaline content. This water completely precipitated copper sulphate out of solution until it became slightly acid, thereafter only a part of the copper was precipitated. The insoluble salt had the general formuak:

$$CuCO_3 \times Cu(OH)_2, \text{ and } CaSO_4.$$

4. The reclaimed precipitate had the same flotative effect as the fresh sulphate with an equal amount of copper. This correlation was made with iron present and with it absent.

5. Beaker tests were made with copper sulphate and metallic iron in the tap water. The precipitate contained copper salts, metallic copper, and hydrolyzed iron. The filtrate contained iron and copper.

6, If a flotation pulp is allowed to become acid undoubtedly metallic iron is injurious, and even if alkalinity is maintained the iron may prove to be a menace.

7. Flotation tests were good when as much as 4 pounds of copper sulphate per ton of ore was used, but when iron was present the results were vitiated. Abraded iron in the flotation circuit should be regarded as a possible deterrent when copper sulphate is used.

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